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ORIGINAL ARTICLE

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Catalytic pyrolysis of cellulose in sulfolane with some acidic catalysts

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Abstract Catalytic pyrolysis of cellulose in sulfolane (tetramethylene sulfone) with sulfuric acid or polyphosphoric acid gave levoglucosenone, furfural, and 5-hydroxymethyl furfural (5-HMF) up to 42.2%, 26.9%, and 8.8% (as mol% yield based on the glucose unit), respectively. Pyrolysis behaviors of the intermediates indicated the conversion pathways, and the conversion: levoglucosenone → furfural was found to require water. The control of the water content in the pyrolysis medium was quite effective in controlling the product selectivity between levoglucosenone and furfural: mild vacuum conditions to remove the product water dramatically enhanced the levoglucosenone yield, while steam distillation conditions increased the furfural and 5-HMF yields.

Key words Cellulose · Catalytic pyrolysis · Acid · Levoglucosenone · Furfural

Introduction

Pyrolysis in sulfolane (tetramethylene sulfone), an aprotic polar solvent, is an effective way to control cellulose pyrolysis for the formation of low molecular-weight (MW) products without forming carbonized residues.¹ This is achieved by inhibiting the polymerization of levoglucosan, which is the important primary pyrolysis product.² In the swollen state of cellulose with sulfolane, the pyrolysis reaction is reported to start from the molecule that is most closely associated with the solvent in a type of peeling reaction, while the molecule that cannot associate with sulfolane is stable even in the noncrystalline region.³ However, the mixture of low MW products obtained from the pyrolysis in sulfolane was also complex and included levoglucosan,

levoglucosenone, furfural, and 5-hydroxymethyl furfural (5-HMF) (Fig. 1) due to the variety of pyrolytic reactions.¹ The use of a catalyst is expected to provide effective control of these pyrolytic reactions.

Following the pioneering works of Tsuchiya and Sumi,⁴ Wodley,⁵ and Lipska and McCasland,⁶ Halpern et al.⁷ identified levoglucosenone (1,6-anhydro-3,4-dideoxy- β -D-glycero-hex-3-enopyranose-2-ulose) in the pyrolysis mixture of cellulose with acidic catalysts including ammonium dihydrogen phosphate, sodium dihydrogen phosphate, and sodium hydrogen sulfate.⁷ After that, many researchers investigated the formation of levoglucosenone^{8–15} and its application as a chiral synthon for the synthesis of various biologically active compounds.^{16,17} Fixed $^1\text{C}_4$ conformation, no hydroxyl groups for protection, the sterically hindered β -D-face, and a reactive α,β -unsaturated carbonyl system are indicated as advantageous points of levoglucosenone as a chiral synthon.¹⁶

In this article, catalytic pyrolysis of cellulose in sulfolane with sulfuric acid or polyphosphoric acid is presented and discussed with the product selectivity.

Experimental

Catalytic pyrolysis in sulfolane

Pyrolysis was conducted in a round flask (30 ml) made of glass with a cooling tube (120 mm long and 14 mm in diameter) for trapping the volatile products attached with a nitrogen bag through a three-way tap as shown in the previous report.² Cellulose sample (cotton, 200–300 mesh, Toyo Roshi) (50 mg) was suspended in sulfolane (mp 27°C, bp 285°C, Nacalai Tesque) (2.0 ml) containing sulfuric acid (0.1 or 1.0 wt%) or polyphosphoric acid (0.1, 1.0, or 5.0 wt%) and was heated at 200–280°C (in an oil bath) after replacing the air in the pyrolysis apparatus with nitrogen. After immediate cooling with air flow for 30 s and subsequently in cold water for 3 min, the flask and cooling tube contents were extracted with tetrahydrofuran (THF) (2.5 ml \times 2) and

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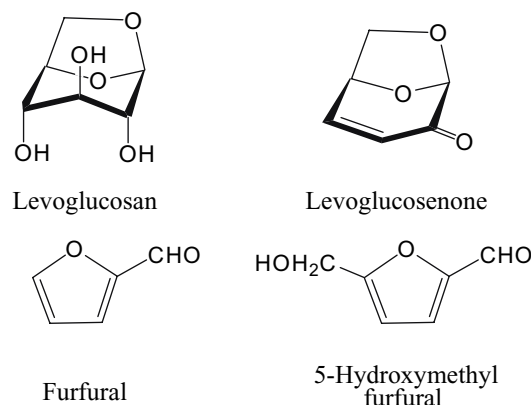


Fig. 1. Low molecular weight products formed in cellulose pyrolysis in sulfolane

the resulting solution was neutralized with solid NaHCO_3 (100 mg). Sulfolane was contained in the THF-soluble portion. Filtration gave soluble and insoluble portions. The insoluble portion was washed with water and dried at 105°C for 24 h to determine the residue mass.

The soluble portion was analyzed with high performance liquid chromatography (HPLC) with *p*-dibromobenzene as an internal standard to determine the yields of levoglucosenone, furfural, and 5-HMF. HPLC analysis was carried out on Shimadzu LC-10A under the following conditions: column, STR ODS-II; column temperature 40°C ; eluent $\text{MeOH}/\text{H}_2\text{O} = 20/80$ ($0 \rightarrow 5$ min), $20/80 \rightarrow 30/70$ ($5 \rightarrow 10$ min), $30/70 \rightarrow 100/0$ ($10 \rightarrow 18$ min); flow rate, 1.0 ml/min; detection at 220 and 254 nm. Yields of levoglucosan and 1,6-anhydro- β -D-glucofuranose were determined by gas chromatography (GC; Shimadzu GC-14B) after acetylation with acetic anhydride and pyridine at room temperature for 24 h. The GC conditions were: column, CBP-5 (25 m \times 0.25 mm in diameter); column temperature, 50°C ($0 \rightarrow 1$ min), $50^\circ \rightarrow 250^\circ\text{C}$ ($1 \rightarrow 21$ min), 250°C ($21 \rightarrow 31$ min); injector temperature, 250°C ; flame ionization detection temperature, 250°C ; carrier gas, He (1.0 ml/min). Proton nuclear magnetic resonance ($^1\text{H-NMR}$) analysis of the extracts with dimethyl sulfoxide- d_6 ($\text{DMSO-}d_6$) including phloroglucinol as an internal standard was also conducted to quantify the products using a Bruker AC-400 FT-NMR spectrometer (400 MHz) with tetramethylsilane (TMS) as an internal standard.

Pyrolysis of levoglucosan, levoglucosenone, furfural, or 5-HMF was conducted in a similar way. Pyrolysis of levoglucosenone in sulfolane (2.0 ml) containing distilled water (0.1 ml) was also conducted.

Vacuum pyrolysis and steam pyrolysis with acidic catalyst

Pyrolysis under nitrogen flow (100 ml/min) at atmospheric or reduced pressure was conducted with the apparatus shown in Fig. 2a. Nitrogen via a mass-flow controller was directly injected into the reaction mixture through a needle. Volatile products were recovered in a THF trap cooled in ice water. The connecting tube between flask and trap was

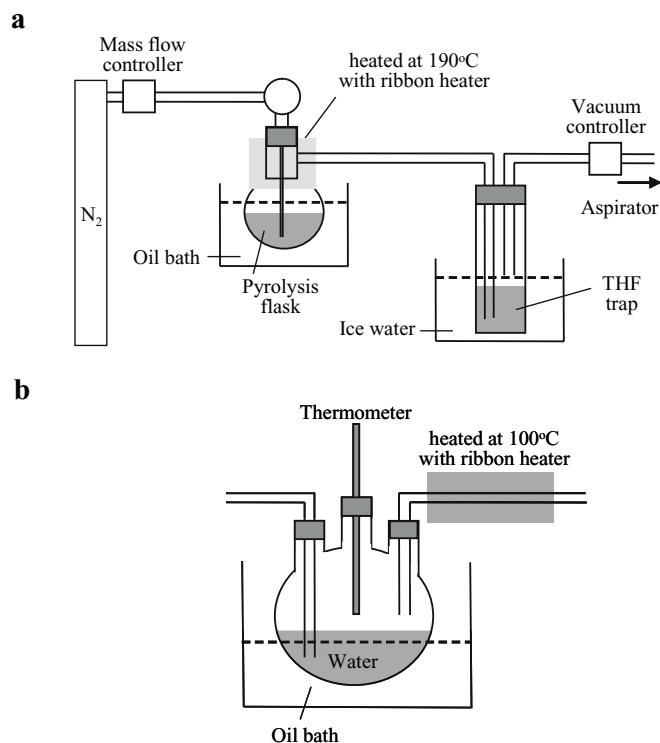


Fig. 2a, b. Pyrolysis apparatus used in the experiments under **a** vacuum and **b** steam distillation conditions

heated at 190°C with a ribbon heater. Vacuum conditions were maintained with an aspirator and a vacuum controller (Okano VCN-500).

Pyrolysis under steam distillation conditions were conducted with a similar apparatus including a steam generator (Fig. 2b) between the mass-flow controller and the pyrolysis flask. In this experiment, flow rates of nitrogen and steam were adjusted to 50 and 60 ml/min, respectively. The connecting tube between the steam generator and the flask was heated at 100°C with a ribbon heater to prevent condensation.

Results and discussion

Formation behavior of levoglucosenone, furfural, and 5-HMF

Catalytic pyrolysis of cellulose in sulfolane containing sulfuric acid or polyphosphoric acid gave levoglucosenone, furfural, and 5-HMF at $200^\circ\text{--}280^\circ\text{C}$. Figure 3 shows examples of the formation behavior of these products at 240°C with polyphosphoric acid (1.0 wt%) or sulfuric acid (0.1 and 1.0 wt%). The pyrolysis time when residual cellulose completely disappeared is also shown in Fig. 3.

Cellulose suspended in sulfolane was consumed much faster with acid catalyst than in the noncatalyzed condition, as indicated by the disappearance times of 60 min (noncatalyzed),¹ 6 min (1.0 wt% polyphosphoric acid), 2 min

(0.1 wt% sulfuric acid), and 1.5 min (1.0 wt% sulfuric acid) at 240°C. These results indicate that acid catalyzes the depolymerization (transglycosylation) reaction.

Maximum yield of levoglucosenone was obtained at the pyrolysis time when residual cellulose was completely consumed except for the case of pyrolysis with 1.0 wt% sulfuric acid, while furfural formation was observed after levoglucosenone formation and with decreasing levoglucosenone yield. This indicates that the conversion pathway: levoglucosenone → furfural exists in this catalytic pyrolysis. Generally, polyphosphoric acid [pK_a 2.15, 7.20 (secondary), 12.38 (tertiary), phosphoric acid],¹⁸ a weak acid, formed levoglucosenone more selectively. On the other hand, with sulfuric acid [pK_a -5.2, 1.99 (secondary)],¹⁸ which is a strong acid, further conversion from levoglucosenone to furfural occurred substantially, and furfural became a major product at the higher acid concentration of 1.0 wt%. Under all conditions, 5-HMF was a minor product.

Yields at the optimized pyrolysis times under various acid concentrations and temperatures are summarized in Table 1. Under the conditions except for 1.0 wt% of sulfuric acid, levoglucosenone was obtained as the main product in 22.3–38.0 mol% of the theoretical yield, while treatment with sulfuric acid (1.0 wt%) at 200° and 240°C gave furfural more selectively in 16.2 and 20.0 mol%, respectively. Such a

high yield of furfural has not been reported in fast pyrolysis of cellulose impregnated with acidic catalyst.

Degradation pathway

Chromatograms obtained from the pyrolysis of levoglucosan, levoglucosenone, furfural, and 5-HMF are shown in Fig. 4 compared with that from cellulose. Very similar chromatograms were obtained from cellulose and levoglucosan pyrolysis. Furthermore, a substantial amount of furfural was formed from levoglucosenone with a small amount of 5-HMF. These results indicate that the pathway: cellulose → levoglucosan → levoglucosenone → furfural exists as a degradation pathway in this catalytic conversion.

Figure 5 shows the change in the product composition for cellulose and levoglucosan pyrolysis. Although ratio between levoglucosenone, furfural, and 5-HMF is very similar, the levoglucosenone/levoglucosan ratio is quite different between cellulose and levoglucosan pyrolysis. For example, the molar ratios after 2 min of pyrolysis are 4.8 and 1.6 for cellulose and levoglucosan pyrolysis, respectively. If levoglucosenone is formed only from levoglucosan, the ratio observed in cellulose pyrolysis should be equal to or even smaller than that in levoglucosan pyrolysis. The ex-

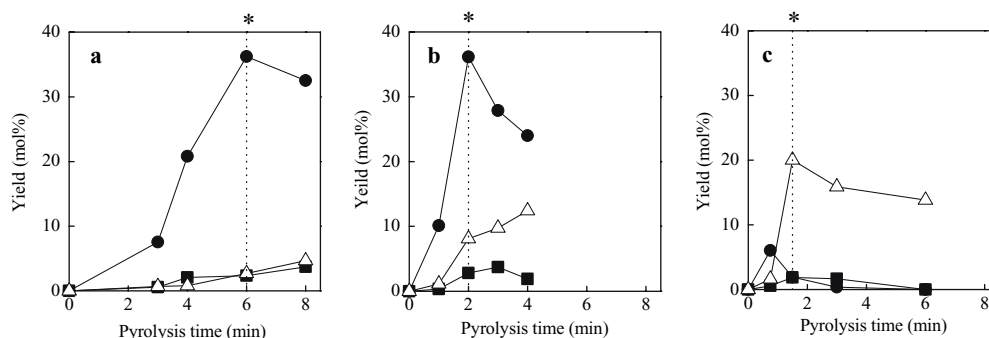


Fig. 3a–c. Change in the yields of levoglucosenone, furfural, and 5-hydroxymethyl furfural (5-HMF) during pyrolysis of cellulose in sulfolane with acid catalyst at 240°C. **a** Polyphosphoric acid (1.0 wt%),

b sulfuric acid (0.1 wt%), **c** sulfuric acid (1.0 wt%). Circles, levoglucosenone; triangles, furfural; squares, 5-HMF; asterisk, pyrolysis time when cellulose residue completely disappeared

Table 1. Yields of levoglucosenone, furfural, and 5-hydroxymethyl furfural (5-HMF) under optimized conditions

Catalyst	Catalyst concentration (wt%)	Pyrolysis temperature (°C)	Pyrolysis time (min)	Yield (mol%)		
				Levoglucosenone	Furfural	5-HMF
Sulfuric acid	0.1	200	4.0	29.9 ^a	ND	2.4
	0.1	240	2.0	36.2 ^a	8.2	2.8
	0.1	280	1.25	33.4 ^a	9.9	4.4
	1.0	200	2.0	4.9	16.2 ^a	3.1
	1.0	240	1.5	1.7	20.0 ^a	2.1
Polyphosphoric acid	0.1	240	60.0	25.4 ^a	3.8	2.4
	0.1	280	5.0	22.3 ^a	2.5	1.5
	1.0	240	6.0	36.2 ^a	2.7	2.5
	1.0	280	2.5	38.0 ^a	5.1	3.9
	5.0	240	4.0	30.6 ^a	2.2	1.4

ND, Not detected

^aOptimized yield

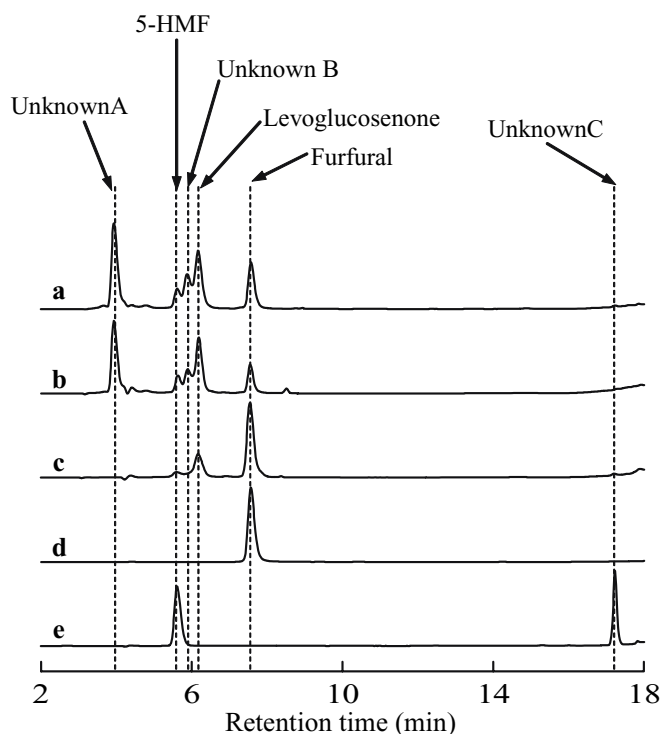


Fig. 4a-e. Chromatograms from high performance liquid chromatography (HPLC) of sulfolane-soluble portions obtained from the pyrolysis of levoglucosan, levoglucosenone, furfural, 5-HMF, and cellulose in sulfolane with sulfuric acid (0.1 wt%). **a** Cellulose (200°C, 2 min), **b** levoglucosan (200°C, 2 min), **c** levoglucosenone (240°C, 3 min), **d** furfural (200°C, 3 min), **e** 5-HMF (200°C, 3 min), all with detection at 254 nm

perimental facts suggest that another pathway also exists in levoglucosenone formation along with the pathway via levoglucosan. Details of this pathway and the relative importance between these pathways are unknown at present, but dehydration prior to levoglucosan formation is also suggested in the pyrolysis of cellulose impregnated with acid catalyst.^{8-10,13} Shafizadeh et al.⁹ reported 1,4:3,6-dianhydro- α -D-glucopyranose as an intermediate for levoglucosenone formation. Dobelet et al.¹³ studied the formation behavior of water and levoglucosenone compared with the retention of the glucose moiety in the pyrolysis residue, and they concluded that dehydration proceeds in the solid state prior to depolymerization.

With addition of water (5.0 wt%), the conversion of levoglucosenone to furfural was dramatically enhanced as shown in Fig. 6. The effect of water can be explained with the proposed mechanism as shown in Fig. 7, which includes hydrolysis via ring opening of the C₁-O₅ bond and elimination of C₆ as formaldehyde before rearrangement into a five-membered ring. Kato and Komorita¹⁹ isolated 3-deoxy-D-xylosone as an intermediate from D-xylose to furfural and they proposed a similar formation mechanism in D-xylose pyrolysis. Houminer and Patai²⁰ reported that C₆ is preferentially split off in pyrolytic conversion of glucose to furfural from the experimental facts that furfural formed from ¹⁴C-labeled glucose only at C₆-position had no radioactivity.

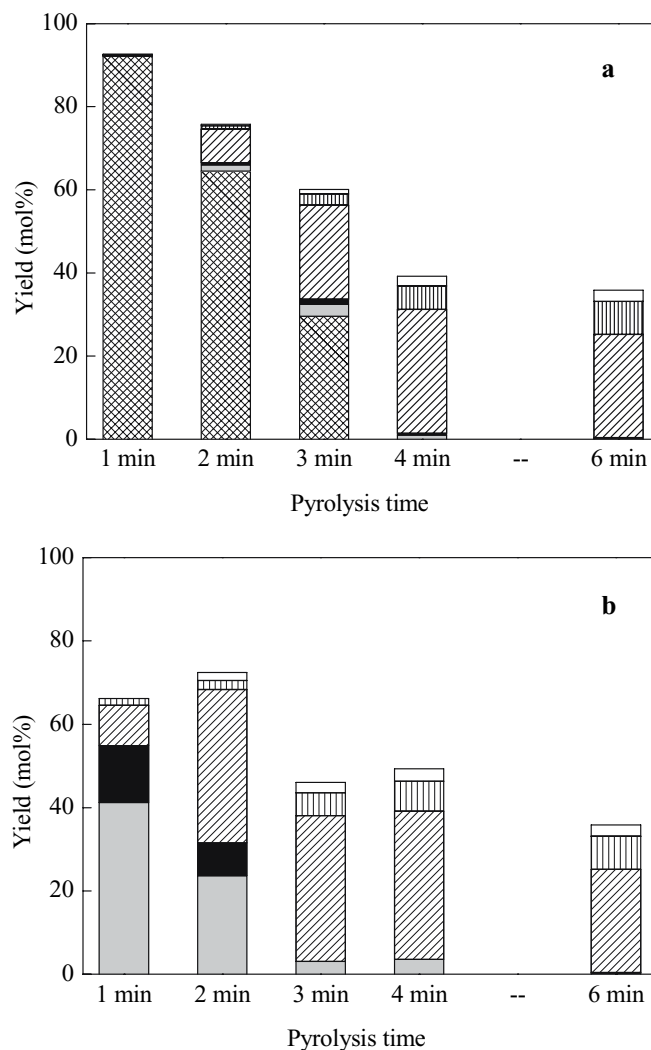


Fig. 5a, b. Change in the product composition during pyrolysis of **a** cellulose and **b** levoglucosan in sulfolane with sulfuric acid (0.1 wt%) at 200°C. Cross-hatched bars, residual cellulose; filled bars, 1,6-anhydro- β -D-glucofuranose; vertically hatched bars, furfural; shaded bars, levoglucosan; obliquely hatched bars, levoglucosenone; open bars, 5-HMF

In this mechanism, attack of water to the oxonium ion intermediate is a key reaction from levoglucosenone to furfural.

Acidity changes depending on the medium. Arnett and Douty²¹ reported the acidity of sulfuric acid in sulfolane by investigating the Hammett acidity function, and they concluded that sulfuric acid in sulfolane has greater acidity than in water. They also reported that a small quantity of water reduces the acidity. Thus, the acidity of sulfuric acid in sulfolane would not increase with addition of water. Therefore, without a nucleophile such as water, the oxonium ion solvated with sulfolane is considered to be transformed to levoglucosenone again through inhibiting the intermolecular reaction such as polymerization. In fast pyrolysis, this oxonium ion may polymerize instead of forming furfural. These different behaviors of the oxonium ion are considered to be the reason why the catalytic pyrolysis in sulfolane gives substantially higher yield of furfural than the fast pyrolysis condition. Furthermore, levoglucosenone as well as

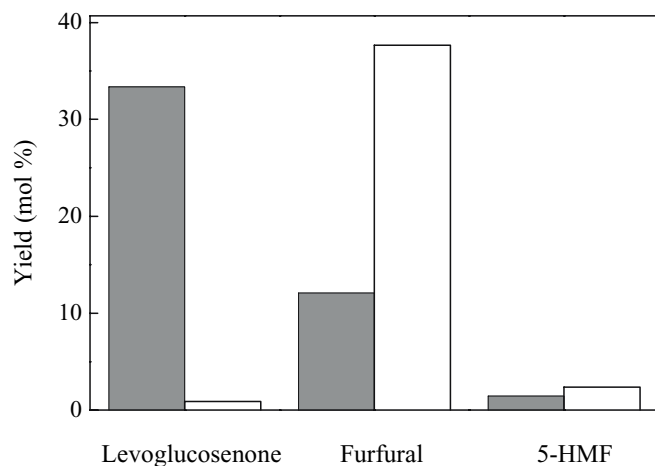


Fig. 6. Effects of water on levoglucosenone pyrolysis in sulfolane with sulfuric acid (0.1 wt%) at 240°C for 3 min. *Shaded bars*, no added water; *open bars*, with water (5 wt%)

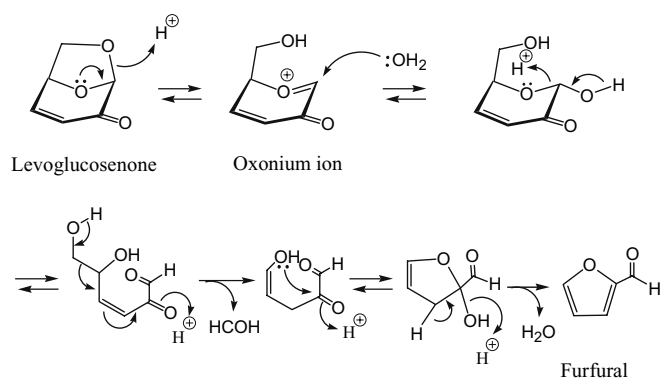


Fig. 7. A conversion pathway from levoglucosenone to furfural

furfural and 5-HMF were found to be fairly stable under the present pyrolysis conditions, as indicated by a small decrease (4.5%) in the total yield of levoglucosenone, furfural, and 5-HMF observed during pyrolysis of cellulose between 4 and 6 min, as shown in Fig. 5a.

1,6-Anhydro- β -D-glucofuranose (AF), which is a furanose-type isomer of levoglucosan, was also formed from levoglucosan as shown in Fig. 5b. Table 2 summarizes the levoglucosan/AF ratio during pyrolysis of cellulose or levoglucosan under various acidic conditions at 200°C. Although AF was not formed from levoglucosan under pyrolysis conditions with no catalyst or with boric acid, polyphosphoric acid and sulfuric acid catalyzed the AF formation to give an equilibrium mixture of levoglucosan and AF (ca. 3:1). A similar equilibrium mixture was also obtained from cellulose. Dry pyrolysis of cellulose is known to form levoglucosan much more selectively than AF, noting that Gardiner²² reported the levoglucosan/AF ratio of 25.6:1 from vacuum pyrolysis of cotton cellulose. Thus, interconversion between levoglucosan and AF occurs under polyphosphoric acid and sulfuric acid conditions through acid-catalyzed ring-opening of the C₁-O₅ bond.

Table 2. Effect of pyrolysis conditions on levoglucosan/1,6-anhydro- β -D-glucofuranose ratio in sulfolane at 200°C

Sample	Catalyst	Pyrolysis time (min)	Levoglucosan/AF
Cellulose	Sulfuric acid (0.1 wt%)	2	75/25
		3	72/28
		4	72/28
		6	72/28
Levoglucosan	No catalyst	2	100/0
	Boric acid (1.0 wt%)	2	100/0
	Polyphosphoric acid (1.0 wt%)	2	74/26
	Sulfuric acid (0.1 wt%)	2	76/24

AF, 1,6-Anhydro- β -D-glucofuranose

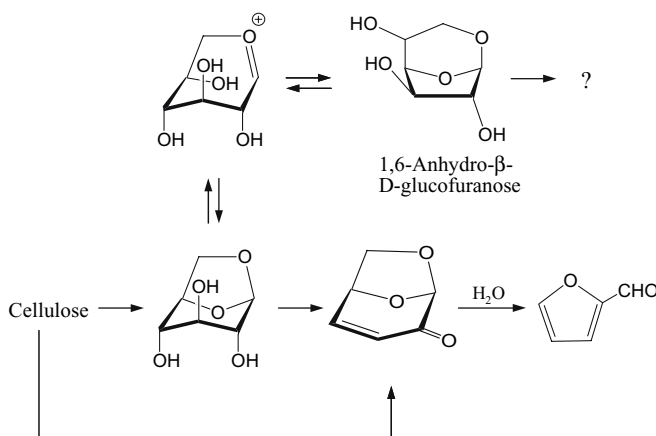


Fig. 8. Pathways in cellulose pyrolysis in sulfolane with acidic catalyst

From these lines of evidence, the degradation pathway of cellulose during pyrolysis in sulfolane with sulfuric acid or polyphosphoric acid is proposed as shown in Fig. 8. Acetal linkages in levoglucosan and levoglucosenone are cleaved through acid-catalyzed ring-opening, while levoglucosenone is expected to have much lower reactivity due to low electron densities of C₅- and C₆-oxygen through the electron-withdrawing tendency of the carbonyl group at the C₂ position. These reactivity differences are considered to work effectively with polyphosphoric acid, a weak acid, to give levoglucosenone more selectively. On the other hand, sulfuric acid, a strong acid, has a tendency to mask these reactivity differences. Formation of 1,6-anhydro- β -D-glucofuranose from levoglucosan is not desirable for levoglucosenone formation, although products from AF are unknown at present.

Vacuum pyrolysis and steam pyrolysis with acidic catalyst

According to the proposed mechanism shown in Figs. 7 and 8, water content is an important factor for determining the product selectivity between levoglucosenone and furfural. During normal catalytic pyrolysis in sulfolane, a substantial amount of water is produced from a dehydration reaction.

Table 3. Effects of vacuum and steam distillation conditions on the product selectivity between levoglucosenone and furfurals

Conditions ^a	Yield (mol%)			
	Levoglucosenone	Furfural	5-HMF	Furfural + 5-HMF
In nitrogen	24.8 (100)	8.0 (100)	3.8 (100)	11.8 (100)
Under nitrogen flow ^b				
1 atm	30.3 (122)	8.6 (108)	0.8 (21)	9.4 (80)
0.1 atm	38.1 (154)	3.8 (48)	0.6 (16)	4.4 (37)
0.1 atm	42.2 (170)	2.3 (29)	0.8 (21)	3.1 (26)
Steam distillation ^c	8.5 (34)	26.9 (336)	8.8 (232)	35.7 (303)

Values in parentheses show relative yield (%) against the yield in nitrogen

^a Sulfuric acid 0.1 wt%/200°C/6 min

^b Flow rate 100 ml/min

^c Nitrogen (50 ml/min) and steam (60 ml/min)

Therefore, removal of the product water could enhance the selectivity of levoglucosenone formation.

Table 3 summarizes the yields of levoglucosenone, furfural, and 5-HMF from cellulose under vacuum and steam distillation conditions (0.1 wt% sulfuric acid/200°C/6 min). The relative yield of levoglucosenone dramatically increased up to 154% and 170% under mild vacuum conditions at 0.16 and 0.12 atm with nitrogen flow with decreasing total yields of furfural and 5-HMF of 37% and 26%, respectively. Nitrogen flow at atmospheric pressure also increased the levoglucosenone yield by 22%. Thus, removal of product water is quite effective to control the product selectivity for the formation of levoglucosenone.

Contrary to this, under steam distillation conditions, furfural (26.9%) and 5-HMF (8.8%) were obtained with the levoglucosenone yield decreasing to 8.5%. The total yield (35.7%) of furfural and 5-HMF is about threefold that obtained in nitrogen. Under steam distillation conditions, most furfural (91.4%) was recovered in the cooling trap, and this also inhibits the further degradation of furfural. From these results, it appears that product selectivity between levoglucosenone and furfurals can be easily controlled through the control of the water content in the pyrolysis mixture.

Conclusions

Formation behaviors and pathways from cellulose to levoglucosenone, furfural, and 5-HMF in acid-catalyzed pyrolysis of cellulose in sulfolane were clarified. Water was found to be a key factor in the conversion of levoglucosenone to furfural, and the product selectivity between these products was effectively controlled by adjusting the water content in the pyrolysis medium through vacuum or steam pyrolysis conditions.

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